Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment

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Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the Upper River Severn catchment

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Abstract

Measurements of pH, alkalinity and electrical conductivity are used to examine the extent of the spatial and temporal variation in stream and ground water chemistry for the Upper Severn catchment, Plynlimon. Wide temporal variations in stream waters broadly reflect flow conditions and complex soil and ground water interactions but not soil type, land usage or geology. The results have major implications for the use of critical load analysis and the development and application of models in upland catchments. They point to the value of field measurements for assessing the environmental management of upland catchments, rather than the present use of over simplistic or inappropriate models.

Introduction

Many parts of the UK uplands have surface waters that are both acidic and acid sensitive. Consequently, in-stream ecology has proved vulnerable to the effects of acidification particularly when associated with acid deposition and land use change (Stoner, *et al.*, 1984; Neal, *et al.*, 1992a; Davies, *et al.*, 1992; Harriman, *et al.*, 1994; Neal, *et al.*, 1997a). Upland catchments are well known for large spatial and temporal stream water quality variation, because of the heterogeneous nature of underlying hydrological and hydrochemical processes (Christophersen, *et al.*, 1993; Neal, *et al.*, 1990a; Robson, *et al.*, 1993; Neal, *et al.*, 1997a). Temporal and spatial variations in stream water chemistry may occur over time scales varying from sub-daily, weekly-yearly or even ten yearly. Spatial variations also occur on various levels increasing from the local (1m), to the reach (100m) or the catchment (10Km) (Blöschl & Sivapalan, 1995). However, the extent of this variability has still not been described to any major degree.

The management of upland aquatic environments requires the development and application of mathematical models to produce reliable working guidelines for the protection of water quality. However, the production of a suitable hydrochemical modelling framework for such areas has proved difficult, for three main reasons (Christophersen, *et al.*, 1993; Neal, *et al.* 1990b; Neal, *et al.*, 1997a; Robson, 1993). Firstly, calibration data rarely provide enough information to identify model parameters. Thus, models can produce a good fit between observations and prediction even though they do not necessarily describe the scale of the dominant hydrological processes and in some cases give unrealistic values for features such as water storage (Christophersen, *et al.*, 1993; Robson, 1993). Secondly, model variables are often difficult to define from field observations because of catchment heterogeneity and/or a conceptual model structure being imposed on the system (Cosby, *et al.*, 1985; Christophersen, *et al.*, 1993). Thirdly, mathematical models simplify processes occurring in the catchment, overlooking the potential importance of intra-catchment variability. The problems associated with current models raise questions concerning their applicability in heterogeneous upland catchments (Christophersen, *et al.*, 1993; Neal, *et al.*, 1997a).

Whilst some field and modelling investigations have examined temporal and spatial variability (Neal, *et al.*, 1990a, 1992b, 1997 a,b,c), major gaps in knowledge remain. The work presented in this paper extends field research by identifying, at much improved temporal and spatial resolution, the chemical variability within catchments based on measurements of pH, alkalinity and conductivity. The work also examines the use of chemical mixing models, (EMMA, End-Member Mixing Analysis) as already applied to upland streams (Neal, *et al.*, 1990a,b;

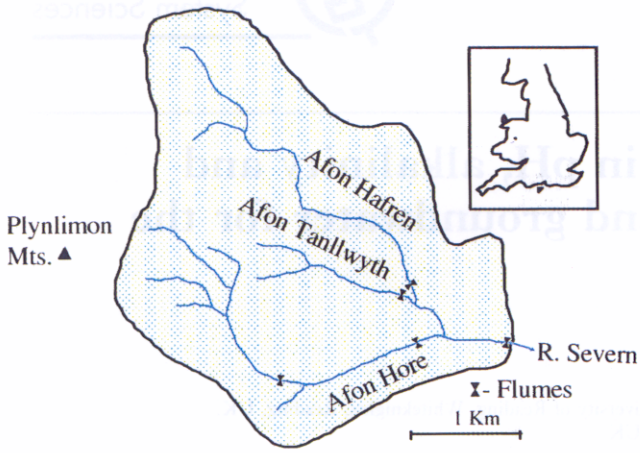

Fig. 1. *Catchment map for the Upper Severn catchment and tributaries*

Christophersen, *et al.*, 1990). From this, a descriptive assessment of the links between measurement and modelling constraints is provided.

Study Area

This investigation is based in the partially forested upper River Severn catchment, Mid-Wales (UK). The area has been the subject of intensive monitoring by the Institute of Hydrology (Plynlimon) since the late 1960s, with an intensive chemical programme initiated in the early 1980s.

The Severn catchment has three major tributaries, the Afon Hafren, Afon Hore and the Afon Tanllwyth with catchment areas of 3.67, 3.08 and 0.89 Km^2 respectively, and a total area of 8.75 Km^2 (Fig. 1). The upper reaches originate on an extensive plateaux, with a total altitudinal range for the catchment of 320–740 m.

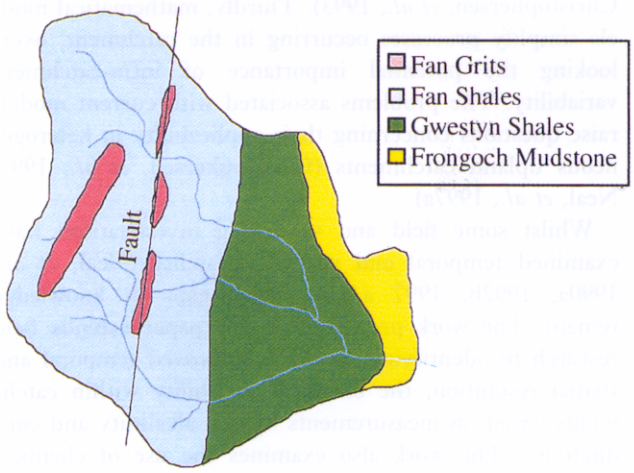

Fig. 2. *Geological Map*

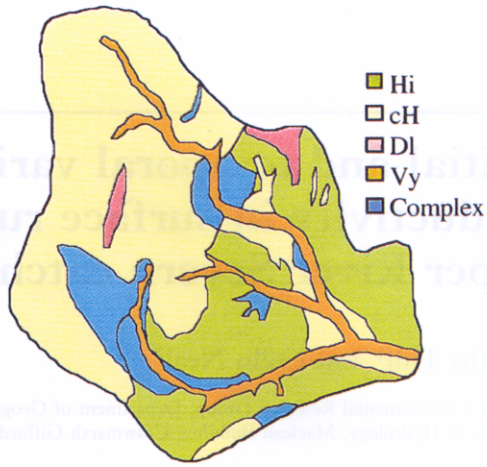

Fig. 3. *Soil Map*
Figure description;

cH Caron Series (Peat, normally >40 cm deep)

Dl Drosgol Association (Peaty podsolised soils usually with strongly developed thin iron pan. Sub-pan characters range from a dark brown humus rich loam to a strongly gleyed silty clay).

Hi Hiraethog (Peaty podsolised soils usually with a well developed thin iron pan over a diffuse ocherous horizon of stony silt-clay loam).

Ya Ynys Series (Peaty gleyed soils).

Vy Valley Complex (Alluvium and soil complexes associated with streams and steep valley sides).

R Rock and Scree.

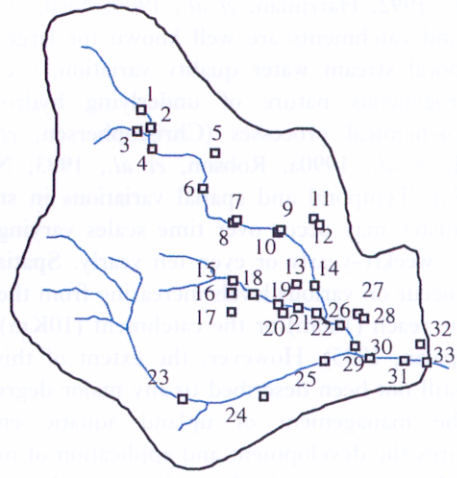

Fig. 4. *Location of sites in the catchment*
Figure description;
see opposite/

Geology

The geology of the Plynlimon massif is that of a complex periclinal inlier exposing uppermost Ordovician and Lower Silurian rocks (Breward, 1990). The Fan Grits (Ordovician) are tough greywacke grits of high quartzose content, with exposures in the upper plateaux area (Fig. 2). Overlaying the grits are the Fan Shales (blue-grey mudstone and shales) which tend to be highly cleaved. At their upper junction with the Gwestyn Shales (Silurian), there is a resistant band, the Rhaeadr mudstone. Gwestyn Shales are grey to black shales and mudstones, containing iron pyrite, weathering to a yellow/brown colour. The Frongoch Mudstones contain little pyrite and consequently are grey in colour. The catchment contains a fault band distinguishable by an outcrop of Fan grits.

Soils

The area is composed of a complex mosaic of stagnopodsol, peat, brown earth and stagno-gley units (Neal, *et al.*, 1997b); the major differences between soil types results from drainage (Fig. 3). Impeded drainage on the plateaux and wider interfluves has led to the accumulation of peat (1–2m deep). On the more freely draining slopes, podsols have developed. A complex of peat and gley mineral soils develop on the valley bottoms due to varying water levels and impeded drainage (Kirby, *et al.*, 1991). On the steeper slopes, there are shallow soils, mainly podsol, with some rock exposures.

Vegetation

Approximately 68 percent of the catchment is commercially managed coniferous forest. Tree varieties include, Norway Spruce (*Picea abies*), Sitka Spruce (*Picea sitchensis*), Lodgepole Pine (*Pinus contorta*), Scots Pine (*Pinus sylvestris*) and Japanese Larch (*Larix kaempferi*) with the majority being Spruce varieties. The main forested area was planted between the late 1930s and 1960s; parts have been felled and are at various stages of replanting. The upper area of the catchment is moorland, vegetated with acidic grassland (*Nardus* and *Festuca*) and peaty mires.

Site Number	Site Name	Site Number	Site Name
1	HAF1	18	TAN4
2	HAF2	19	TAN5
3	HAF3	20	TAN6
4	HAF4	21	TAN7
5	HAF5	22	TAN8
6	HAF6	23	HOR1
7	HAF7	24	HOR2
8	HAF8	25	HOR3
9	HAF9	26	SEV1
10	HAF10	27	SEV2
11	HAF11	28	SEV3
12	HAF12	29	SEV4
13	HAF13	30	SEV5
14	HAF14	31	SEV6
15	TAN1	32	SEV7
16	TAN2	33	SEV8
17	TAN3		

Climate

Average rainfall is approximately 2518 mm/year, with evaporation and transpiration losses 500 to 700 mm/year; snow forms 5 percent of annual precipitation, however, these values are variable. The average annual temperature is 7.3°C, with an average annual minimum and maximum of 3.7°C and 11.0°C, respectively.

Sampling Strategy

Since the early 1980s, weekly chemical data have been collected for five main stream sites in the Severn catchment. The upper and lower Hore, Tanllwyth and lower Hafren sites were located adjacent to flumes, with an additional site at the upper Hafren on the boundary between moorland and forest. Over the past four years, the network of monitoring sites has extended substantially to examine the importance of groundwater and soil water sources to streamflow generation (Neal, *et al.*, 1997 b,c). This study utilises the existing network of stream and ground water monitoring points, extending further the number of sampling points and the frequency of sampling.

For the surface water sites, greater spatial resolution is achieved by sampling a large number of sites, while temporal resolution is improved by sampling at higher frequency for a selected site (HAF14). Weekly data were collected at thirty-three stream sampling points for two or more years, most exceeding three years (Fig. 4). The stream sites, on differing geology, soil type, land usage and flow duration, are named in relation to two factors. The main sub-catchments, HAF(Hafren), HOR(Hore), TAN(Tanllwyth) and SEV(Severn) and a numerical system with increasing order downstream (details of alternative site names used in other publications are given in Appendix 1). For the groundwater system, twenty boreholes in the catchment were sampled weekly for over one year and, for a selected site (LS4), increased temporal resolution was achieved by more frequent sampling. A description and map of the borehole network with further details can be found in Neal, *et al.*, 1997c.

Chemical Techniques

The sampling and analysis of the rainfall and main rivers are described in earlier papers. In essence wide ranging major, minor and trace elements have been determined for weekly samples. For the groundwater, a preliminary survey of the major, minor and trace elements with lower ana-

lytical resolution was undertaken (Neal, *et al.*, 1997c.) based on monthly samples.

For this study, at each site, temperature, pH, conductivity and alkalinity are measured. Temperature is measured in the field using a glass thermometer with an accuracy of 0.1°C, at 25°C. To prevent deterioration of the sample, due to carbon dioxide degassing, the water samples are kept in sealed airtight bottles and analysed for pH, conductivity and alkalinity on return to the laboratory. The pH is measured using a temperature-compensated combined *Radiometer* meter and electrode system (PHM92) with an accuracy of 0.02 pH units, which was validated, on the day of measurement, by a standard 10^{-4}N H_2SO_4 solution. The conductivity is measured using a temperature-compensated *Jenway* (Model 4000) meter and electrode system. Alkalinity is determined by modified Gran titration using a *Metrohm* auto-titration system and is defined as the partial sum of the proton consuming buffers minus the hydrogen ion activity. Two alkalinity values are measured, a low acid volume alkalinity representing the linear Gran function (pH range 4.50–4.00) and a high acid volume alkalinity (pH range 4.00–3.00). The two ranges were chosen to examine the partial pressure of CO_2 and the alkalinity component associated with organic acids. In the pH range of 4.5–4.0, where the dominant buffering component is bicarbonate, the alkalinity can be expressed in the form (Neal, 1988a);

$$Alk_{4.5-4.0} \approx HCO_3^- - H^+ \quad (1)$$

(where all concentrations are given in (Eql^{-1})

An assessment of the bicarbonate concentration with relation to the alkalinity and pH enables an estimate to be made of the excess partial pressure of CO_2 ($EpCO_2$) from the formula (Neal, 1988b);

$$EpCO_2 \approx \{(Alk_{4.5-4.0} + H^+).H^+\} \approx \{(HCO_3).H^+\}/6.25 \quad (2)$$

(where all concentrations are given in (Eql^{-1})

For the lower alkalinity pH range, organic anions ($HOrg^-$) are potentially important as,

$$Alk_{4.0-3.0} \approx HCO_3 + HOrg^- - H^+ \quad (3)$$

(where all concentrations are given in (Eql^{-1})

However, in practice the organic acid buffering component is small and the two measures of alkalinity are similar. For the present study, only the data for the lower pH range alkalinity ($Alk_{4.0-3.0}$) are included. To compare the pH of groundwater with that of the surface runoff, allowance is made for the differences in dissolved carbon dioxide, between the high pCO_2 groundwater ((50 times atmosphere) and stream waters that are approximately in equilibrium with the atmosphere. For example, the groundwater with the highest pH has a value of 6.8, but this increases to 8.9 on standing and equilibration with the atmosphere. To allow for this difference, the pH values were normalised to equilibrium with the atmospheric CO_2 (pH[degassed]), and is calculated using Equation 2.

Results

TEMPORAL VARIATIONS IN SURFACE WATERS

Chemical sampling is usually undertaken at lower frequencies than the time scales at which the hydrological processes operate; measurements on a weekly or monthly basis may fail to identify the chemical dynamics during short period events. To represent the general patterns in a concise manner, one site (HAF14) is examined in detail. Initial analysis revealed that the most dominant temporal feature was the effect on the chemistry caused by flow. Consequently, in this paper, emphasis is placed on this aspect with the chemical data plotted with discharge and time.

Event-Based Variations in Surface Waters

The short-term temporal variations in stream water chemistry reflect the relative contributions of soil and ground water, and are related both to instantaneous flow and antecedent flow conditions (Fig. 5). Prior to a high flow event, pH and alkalinity are high (6.0–6.5; 20–30 μEql^{-1} respectively) with low conductivity, (37–40 μScm^{-1}) reflecting the larger relative contribution from groundwater. With the onset of an event, pH and alkalinity decline rapidly to approximately 4.5 and minus 40 μEql^{-1} with the conductivity rising to 70 μScm^{-1}, as the groundwater contribution decreases. A hysteresis effect is observed when subsequent larger flow events do not cause such large changes in pH, alkalinity or conductivity. Under persistent high flow conditions, conductivity may decrease as rainwater displaces pre-event water, to a large degree, in the soil water system. Throughout the study period, the pH and alkalinity are controlled by the flow conditions. However, while conductivity, in general, increases with flow, the relationship is weak. These relationships are consistent with the conceptual framework outlined by using end-member mixing analysis (EMMA). Thus, total flow reflects the groundwater and soilwater contribution, with low flows being dominated by groundwater and high flows by soilwater. The resultant stream chemistry reflects the hydrology, low flows having higher concentrations of weatherable base cations and high flows having higher concentrations of acidic soil water components.

Daily/Weekly Variations in Surface Waters

The patterns observed between flow and chemistry on the short-time scales are repeated for the longer time scales. Both pH and alkalinity are strongly correlated with discharge, while conductivity has a less clear relationship (Figs. 6 & 7). A large amount of scatter is observed in the daily and weekly sampled data, with no hysteresis effect overall.

Long-Term Trends in Surface Waters

A seasonal variation is observed for pH and alkalinity with winter minima and summer maxima, again, reflecting the

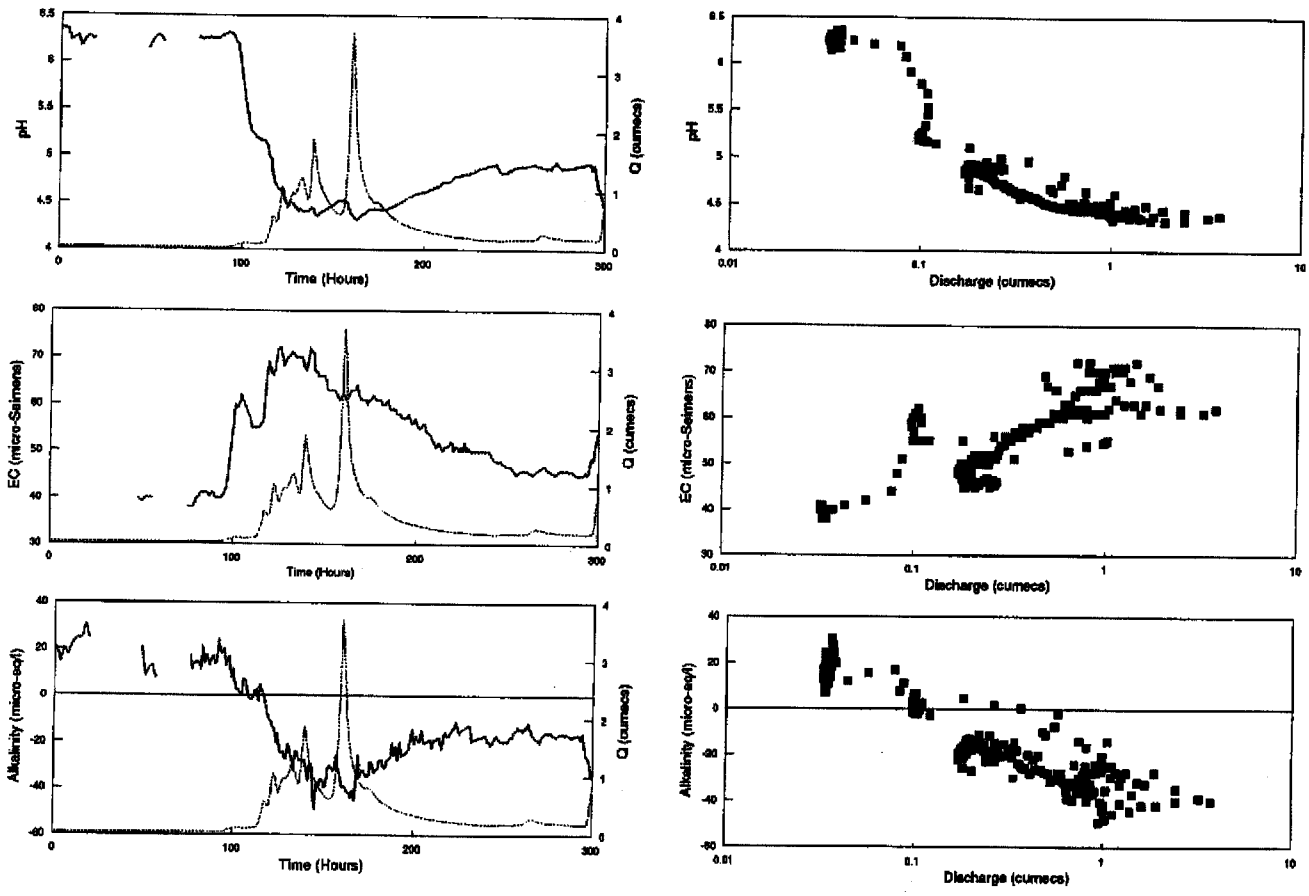

Fig. 5. *Hourly variations in pH, EC and alkalinity in response to an individual, but large flow event. Also plotted is pH, EC and alkalinity with the log of discharge.*

inverse relationship with flow. Conductivity, generally, exhibits a positive relationship but, the pattern is significantly masked by scatter. No long term trend for pH or alkalinity has been observed at Plynlimon (Robson & Neal, 1996).

TEMPORAL VARIATIONS IN GROUNDWATER

Prior to this investigation, the temporal variation in groundwater chemistry had not been assessed. As with the surface waters, one site (LS4) was selected and sampled at a high temporal resolution to represent the behaviour of groundwater. Chemical data were plotted against time and water level to examine the variation resulting from varying flow conditions. The use of EMMA to evaluate stream chemistry requires a homogeneous groundwater end-member composition, (Neal, *et al.*, 1997a) and the results presented here are used to examine this assumption.

Event-Based Variations in Groundwater

At present no chemical data have been collected at hourly intervals. However, groundwater levels react rapidly in response to a rainfall event, suggesting a highly dynamic hydrological system. When compared with stream discharge, groundwater levels have a smoothed response with a noticeable lag time, inferring a dynamic hydrochemical system (Fig. 8).

Daily/Weekly Variations in Groundwater

Two patterns of behaviour are observed between pH/alkalinity/conductivity and water level (Figs. 9 & 10). When the groundwater level is shallow, concentration values show little scatter and pH, alkalinity and conductivity have almost constant values. At greater depth, the scatter is far greater and the values higher. For the shallower levels, there is a dynamic response in water level due to the changing hydrological conditions. However, the lack of response in the chemical characteristics indicates a steady-state system, with regard to weathering and mixing reactions. At deeper levels, flows are low resulting in borehole chemistry being controlled by weathering kinetics and residence times.

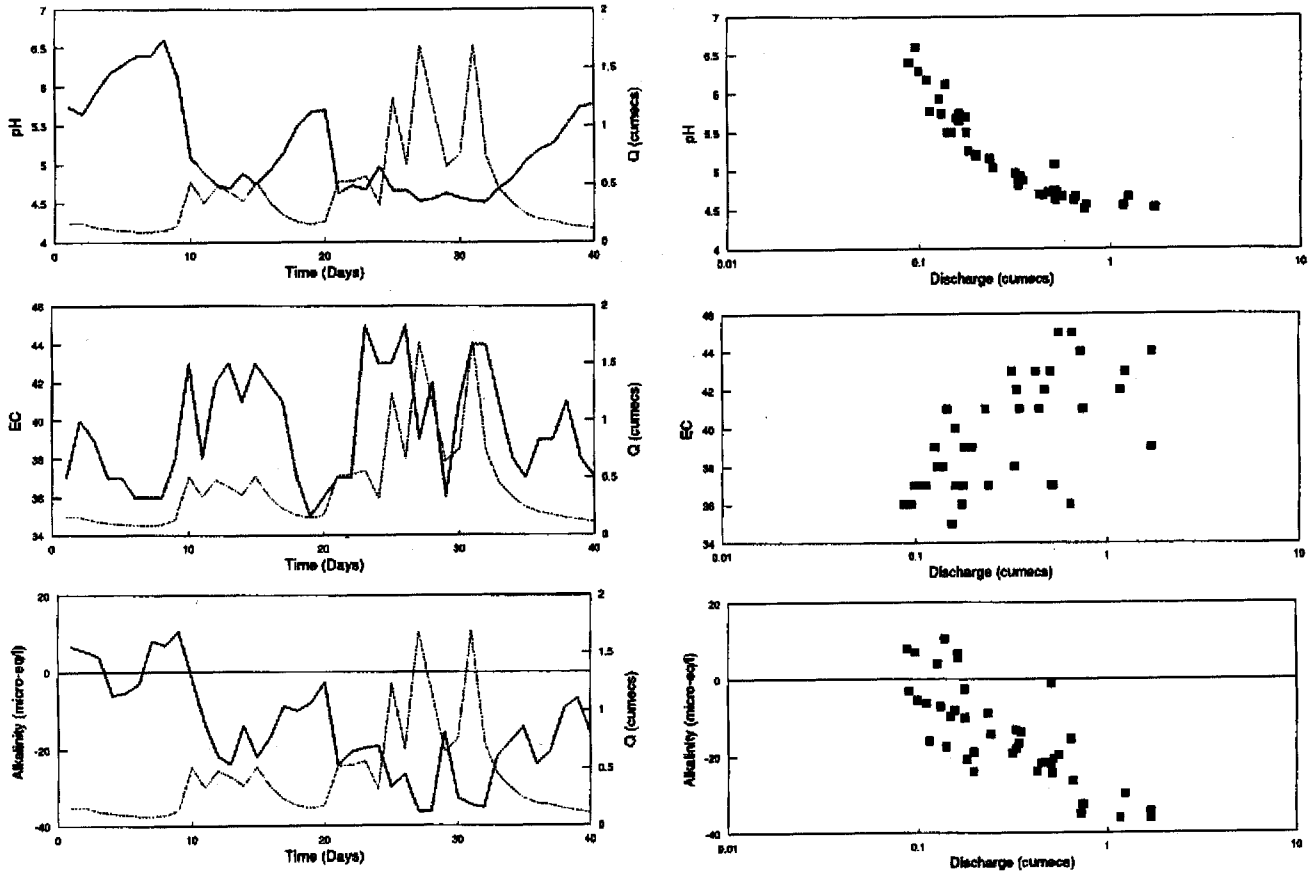

Fig. 6. *Daily variations in pH, EC and alkalinity, pH, EC and alkalinity are also plotted with the log of discharge.*

Long Term Trends in Groundwater

Strong seasonal patterns are observed with summer maxima and winter minima for pH, conductivity and alkalinity. Summer storm events can decrease the pH, conductivity and alkalinity significantly indicating the importance of summer recharge. Longer period trends in chemistry cannot be examined due to the limitations of a three year data set.

SPATIAL VARIATIONS IN STREAMWATER CHEMISTRY

For the local scale variations, a single study was undertaken on four discrete small streams (Fig. 4); SEV7, SEV2, HAF13 and TAN6, with sampling occurring every twenty to thirty metres downstream from their source. Sites varied from the main perennial stream channels to smaller ephemeral streams located on various soil, vegetation and geological units. Averaged chemical data and extreme range values have been examined to determine the nature of the variation.

Local Scale Variation

Downstream variations in stream chemistry were observed in the four streams investigated, with significant changes occurring along reach lengths (Table 1). For the acidic sites, HAF13 and TAN6, downstream changes are relatively small. HAF13 has a pattern of increasing pH/alkalinity downstream but no discernible pattern for conductivity, whereas TAN6 shows no obvious pattern. For the less acidic sites, SEV2 and SEV7, the downstream changes are larger, with pH/alkalinity decreasing. The changes in the pH and alkalinity relate to the proportionate input of groundwater and soil water sources. Near the headwaters of SEV2, SEV7 and HAF13, an input of less acidic water causes an increase in both pH and alkalinity. Similar downstream changes have also been recorded in other studies, and are generally attributed to the degassing of carbon dioxide from soilwater as it enters the stream (Billet, *et al.*, 1996). However, this cannot be the only reason as the alkalinity would not be expected to change with degassing; at these moderate pH values and calcium concentrations, calcium carbonate precipitation, which would also change the alkalinity, would not be expected.

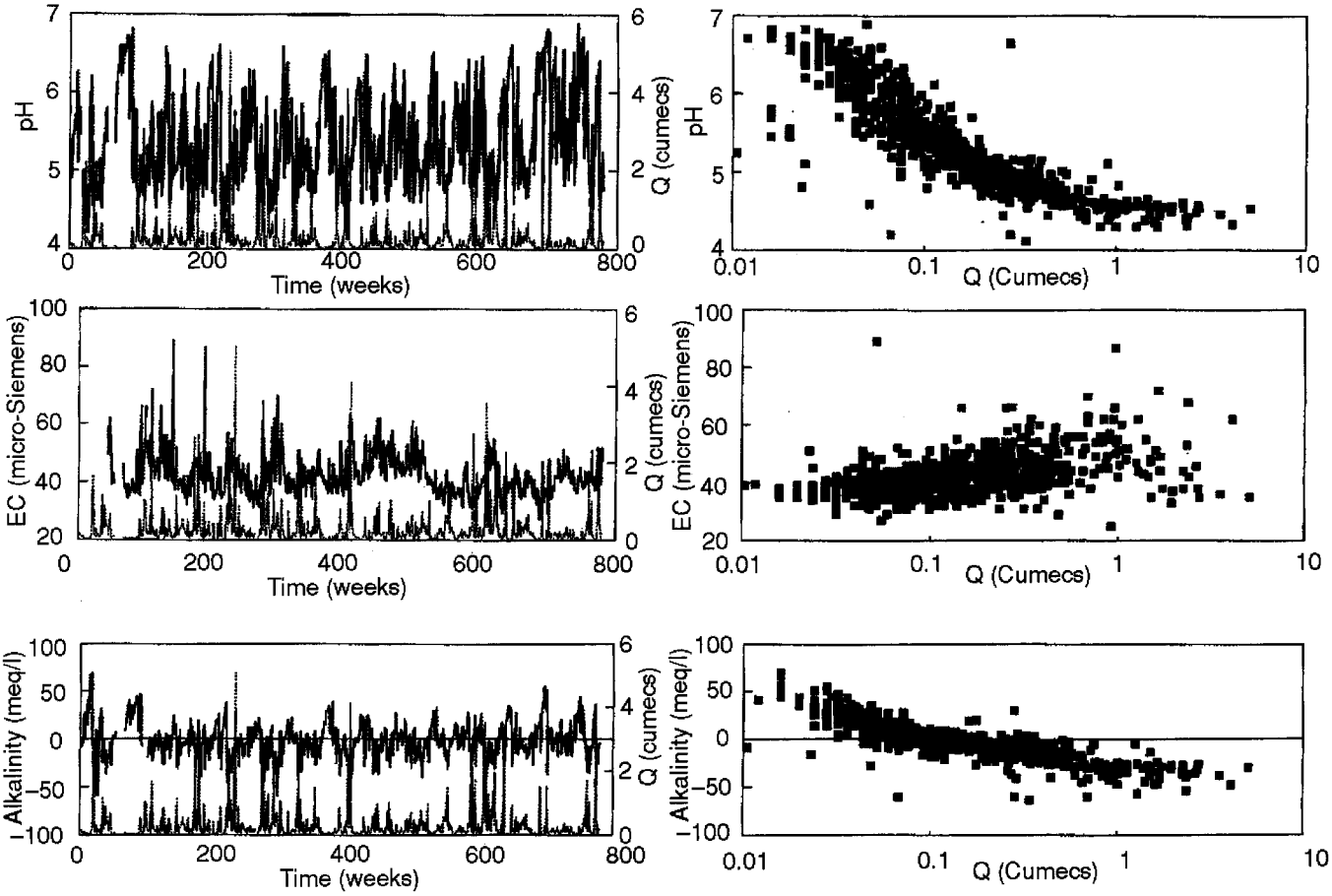

Fig. 7. *Weekly variations in pH, EC and alkalinity, pH, EC and alkalinity are also plotted with the log of discharge.*

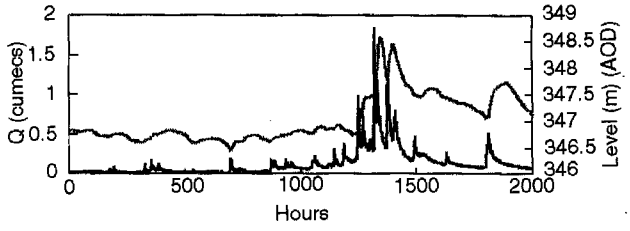

Fig. 8. *Quarter-hourly flow from the Hafren Flume gauging structure plotted with the appropriate levels from the LS5 borehole some 20m from the LS4 borehole, indicating the groundwater response to a high flow event.*

Reach Scale Variation

Between sub-catchments, large spatial variation in pH, alkalinity and conductivity is noted (Table 2 & Fig. 11). Thus, even adjacent streams with similar geology, soil type and vegetation may have differing chemistries. For example, SEV2 and SEV3, located 30 metres apart, respectively have an average pH of 6.43 and 4.77, with an alkalinity of 48 and −19 μEql^{-1}. However, other small streams (e.g. Tan2 & Tan3), again with similar soil type, vegetation and geology have comparable pH, conductivity and alkalinity values (Table 2).

For the main streams, upper and lower Hafren, Tanllwyth and Hore, the upper Tanllwyth is particularly acidic, although the lower Tanllwyth has recently become less acidic due to increased groundwater contribution after the drilling of a borehole increased groundwater fracture routes to the channel (Neal, *et al.*, 1997 b,c). The average pH, conductivity and alkalinity all increase downstream, with the upper reaches having the lowest values. Generally, the main streams have positive alkalinity, the exception being the upper Tanllwyth.

Catchment Scale Variation

Large variation in stream chemistry occurs within the catchment, with the pH, conductivity and alkalinity ranging from 3.58 to 7.66, 22 to 148 μScm^{-1} and −205 to 571 μEql^{-1}, respectively (Table 2; Fig. 11). The large variation across the catchment is coarsely related to the soil type, vegetation or geology, as the most acidic streams tend to be ephemeral and are found on predominantly gley soil e.g. HAF13 and TAN6. The pH, conductivity and alkalinity increase downstream, although the increase is non-linear (Fig. 13), relating to inputs from groundwater and/or well-buffered tributary streams. No significant change in pH or alkalinity is observed in the main

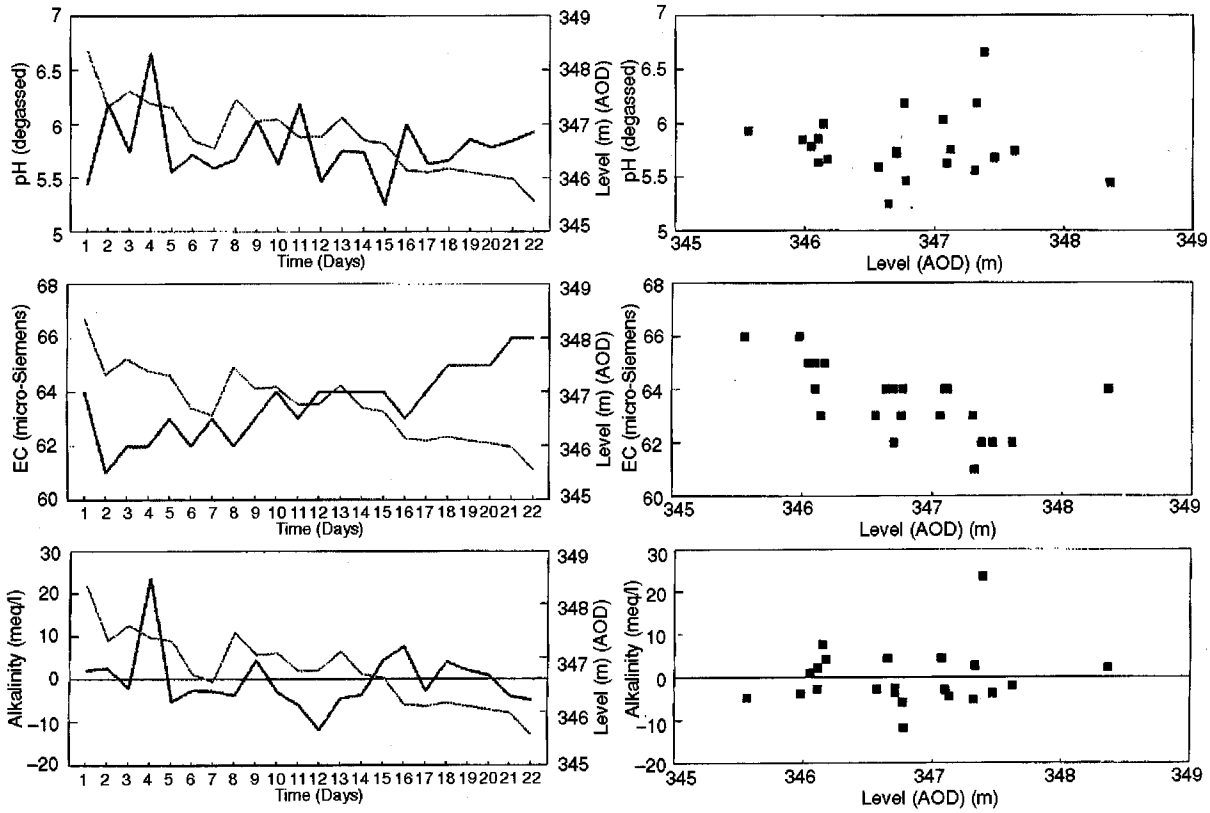

Fig. 9. *Daily variations in pH, EC and alkalinity for the LS4 borehole, also plotted is the pH, EC and alkalinity with level.*

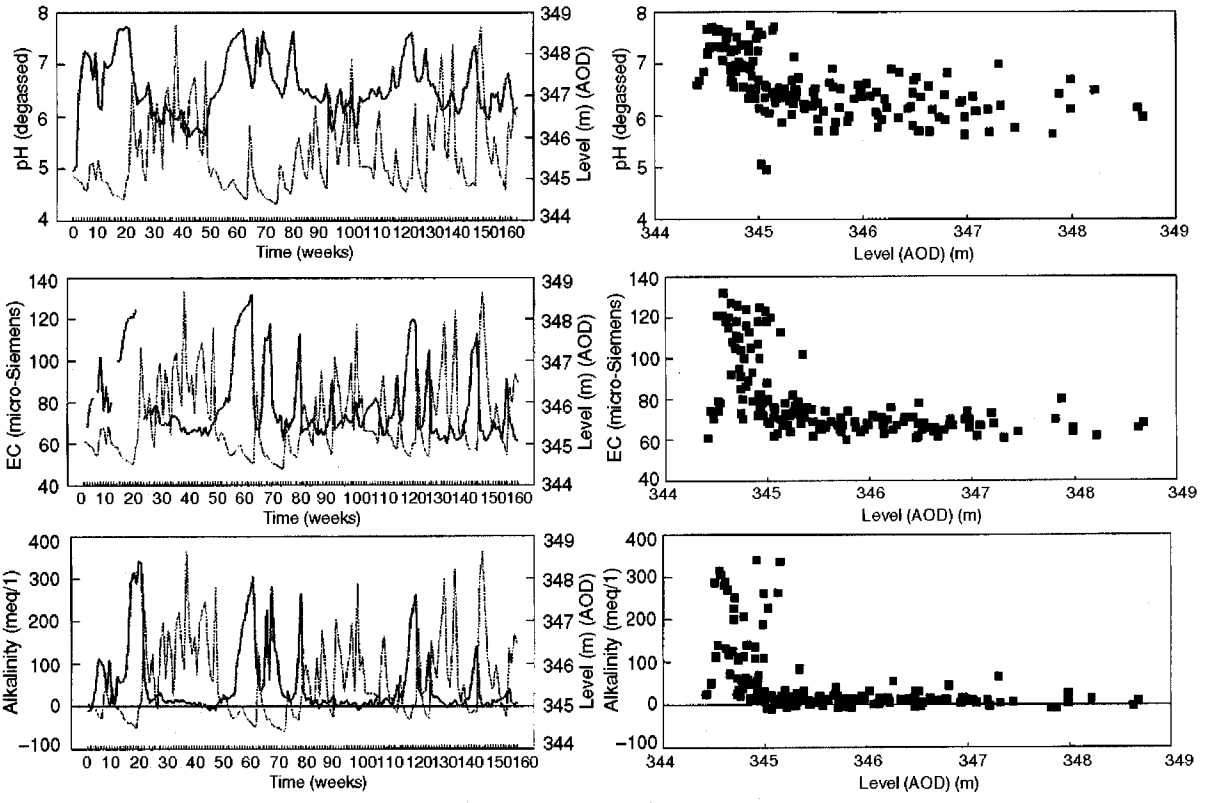

Fig. 10. *Weekly variations in pH, EC and alkalinity for the LS4 borehole, also plotted is the pH, EC and alkalinity with level.*

Table 1.

Site	Temp	pH	EC	Alkalinity
Sev7				
1	6.2	5.42	41	21
2	4.9	5.59	48	–4
3	5.1	5.72	49	–7
4	5.1	5.79	50	–4
5	5.1	5.69	51	–11
6	5.0	5.60	52	–2
7	5.0	5.65	54	–10
8	5.0	5.63	54	–15
Sev2				
1	6.9	5.39	64	–8
2	7.4	5.64	67	22
3	6.7	5.80	63	10
4	5.9	5.65	63	–10
5	5.8	5.40	64	–6
6	5.7	4.76	65	–27
7	5.5	4.63	67	–30
8	5.5	4.62	69	–30
Haf13				
1	4.5	3.97	74	–127
2	4.8	4.02	58	–103
3	4.6	3.97	69	–114
4	4.6	3.96	70	–114
5	4.7	3.92	69	–126
6	4.7	3.94	74	–122
7	4.7	3.96	73	–122
8	4.8	4.13	65	–82
Tan6				
1	5.3	4.08	64	–86
2	5.2	4.08	64	–87
3	5.0	4.09	64	–87
4	5.0	4.08	64	–83
5	5.0	4.11	63	–86

channels as a result of small stream acidic input. The minimum pH values in most streams are relatively constant (pH≈4.0 to 4.5). Therefore, the largest range in pH occurs in streams with higher maximum pHs, indicating the importance of the variability in rates of weathering reactions within the groundwater in determining stream chemistry. The pattern in the minimum and maximum pH values is also found for alkalinity, but not conductivity.

SPATIAL VARIATIONS IN GROUNDWATER CHEMISTRY

To distinguish between spatial changes and those resulting from drilling depth, the boreholes can be divided into 'shallow' (less than 20m deep) and 'deep' (50m deep). Weekly data are used to examine the spatial variation. Local scale variation is examined using two borehole series (US1, US2, US3 and LS1, LS2, LS3, LS4). For the catchment scale changes, all the boreholes are used.

Local Scale Variation

Unexpectedly, large variation was found in pH, alkalinity and conductivity for the groundwater system over small distances (Table 3 & Fig. 12). No general pattern can be found when examining boreholes within a series, with spatial changes being unrelated to location downslope. However, in general, increased mineralisation occurs with greater depth; although LS2 is an exception. The variation at these small scales indicates that the groundwater is highly heterogeneous in composition, probably reflecting the hydrological routing of water which in turn influences the evolution of the groundwater.

Catchment Scale Variation

The large variation found at small scales is reflected at the catchment scale (Fig. 14). Groundwater chemistries are highly heterogeneous, with several factors affecting the composition. Mean pH, conductivity and alkalinity range from 4.6 to 7.4, 40 to 347 μScm^{-1} and minus 12 to 3700 μEql^{-1}, respectively. The role of the geology in determining the groundwater composition can be observed when comparison is made with the groundwater found in the grits and the shales/mudstones: the lowest pH, alkalinity and conductivity occur in the grits. Depth is also an important factor in determining groundwater composition with the 'deep' boreholes (VB2, VB3 & LS6) having the highest pH, alkalinity and conductivity. Although the general composition of groundwater can be explained by the depth of the borehole and the local geology, other boreholes have more anomalous behaviour. For example, IS3 and LS2 boreholes have unexpectedly high pH, alkalinity and conductivity values, with no apparent cause.

Discussion

Both the streamwater and groundwater systems have highly heterogeneous chemical compositions at all temporal and spatial scales. Temporal variations in stream waters reflect the flow conditions, although some hysteresis is observed on short time scales. The temporal variation in groundwater is masked by hydrological pathway changes and increased mineralisation at greater depth.

The spatial variation in both the stream and ground waters is complex. Small scale spatial variations cannot be explained fully by soil type, geology, vegetation cover or geomorphological features, but are a complex interaction of factors, including hydrological and hydrochemical processes. The spatial variation in groundwater is also the result of a complex relationship between various factors, including the geology, the degree of fracturing affecting

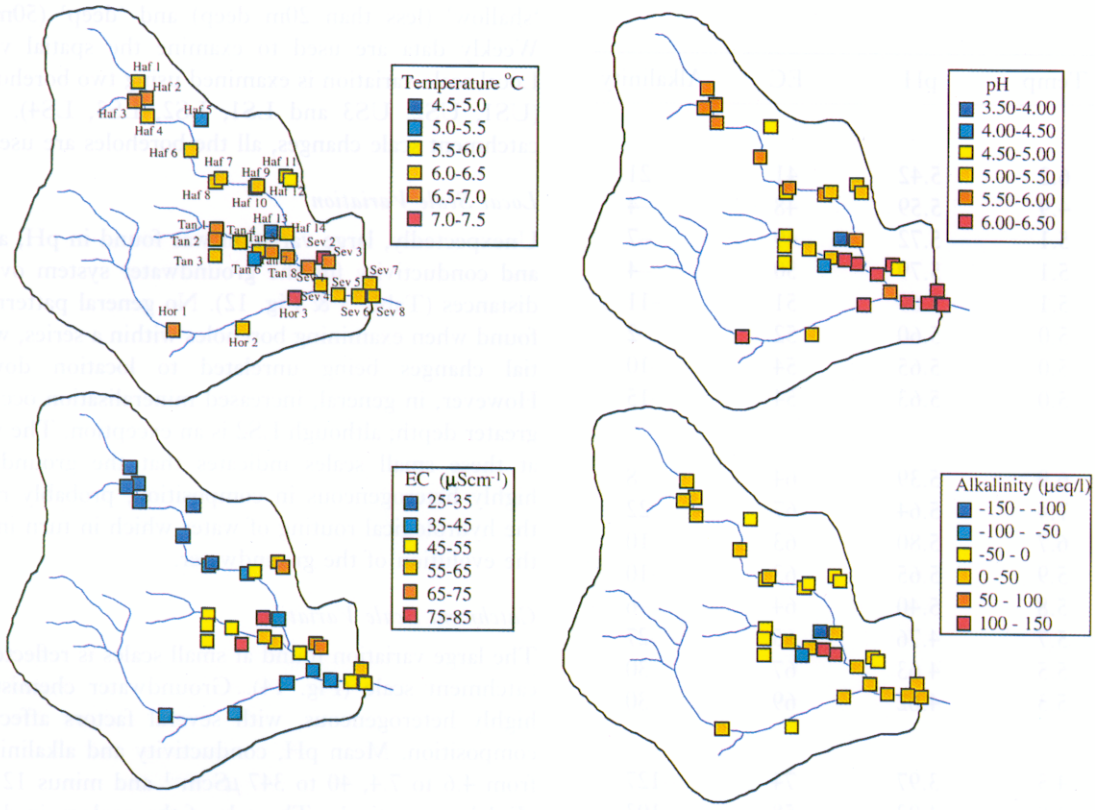

Fig. 11. *Mean spatial variations in stream chemistry across the catchment.*

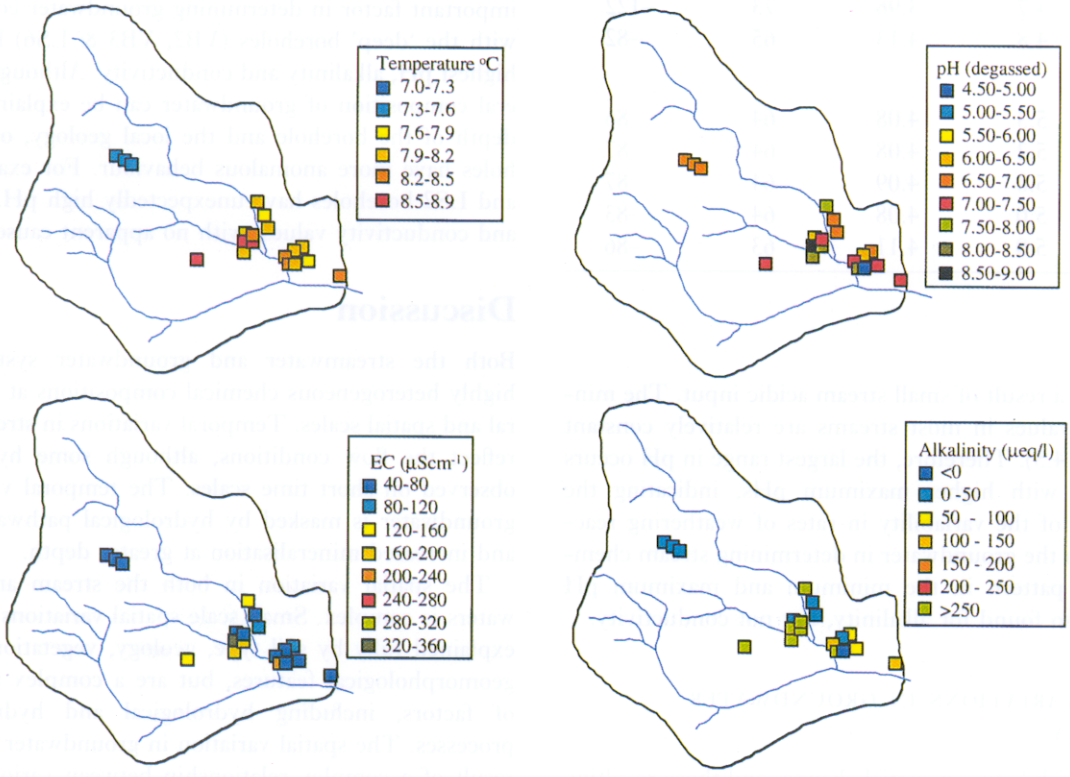

Fig. 12. *Mean spatial variation in borehole chemistry across the catchment.*

Table 2.

Site	Temp	pH	EC	Alkalinity	Geology	Soil Type	Vegetation	Regime
HAF 1								
Min	1.3	4.41	27	–48.0	Fan Shales	Peat	Acid	Perennial
Max	11.1	6.26	48	55.5	& Fan Grits		Moorland	Main River
Range	9.8	1.85	21	103.5				
Mean	**6.4**	**5.56**	**32**	**7.7**				
HAF 2								
Min	1.2	4.45	22	–34.9	Fan Shales	Peat	Acid	Perennial
Max	11.6	7.16	52	52.8	& Fan Grits		Moorland	Main River
Range	10.4	2.71	30	87.7				
Mean	**6.5**	**5.75**	**32**	**8.2**				
HAF 3								
Min	1.1	4.65	27	–33.0	Fan Shales	Peat	Acid	Perennial
Max	12.5	6.24	37	27.4	& Fan Grits		Moorland	Main
Range	11.4	1.59	10	60.4				Tributary
Mean	**6.7**	**5.68**	**30**	**2.7**				
HAF 4								
Min	0.8	4.58	27	–38.0	Fan Shales	Peat	Acid	Perennial
Max	11.5	6.62	39	41.9	& Fan Grits		Moorland	Main River
Range	10.7	2.04	12	79.9				
Mean	**6.5**	**5.84**	**31**	**5.7**				
HAF 5								
Min	0.1	4.17	30	–60.4	Fan Shales	Peat	Acid	Ephemeral
Max	11.4	4.94	53	–3.8			Moorland	Small Stream
Range	11.3	0.77	23	56.6				
Mean	**5.8**	**4.52**	**39**	**–32.2**				
HAF 6								
Min	0.5	4.54	29	–30.5	Fan Shales	Complex	Mature	Perennial
Max	12.4	6.70	44	41.2		Peat/Podsol/	Coniferous	Main River
Range	11.9	2.16	15	71.7		Gley	Forest	
Mean	**6.6**	**5.76**	**33**	**3.5**				
HAF 7								
Min	0.1	4.51	30	–34.9	Fan Shales	Complex	Mature	Perennial
Max	12.5	6.85	45	43.9		Peat/Podsol/	Coniferous	Main River
Range	12.4	2.34	15	78.8		Gley	Forest	
Mean	**6.3**	**5.70**	**34**	**3.1**				
HAF 8								
Min	0.6	4.31	33	–44.5	Fan Shales	Complex	Mature	Ephemeral
Max	13.2	5.72	53	30.9		Peat/Podsol/	Coniferous	Small Stream
Range	12.6	1.41	20	75.4		Gley	Forest	
Mean	**6.2**	**4.66**	**43**	**–21.8**				
HAF 9								
Min	0.1	4.44	30	–31.5	Gwestyn	Complex	Felled &	Perennial
Max	12.0	6.30	60	32.6	Shales	Peat/Podsol/	Replanted	Small Stream
Range	11.9	1.86	30	64.1		Alluvial/Gley	Coniferous	
Mean	**6.3**	**5.18**	**49**	**–5.0**			Forest	
HAF 10								
Min	0.1	4.46	31	–36.1	Gwestyn	Complex	Mature	Perennial
Max	13.8	6.61	52	44.2	Shales	Peat/Podsol/	Coniferous	Main River
Range	13.7	2.15	21	80.3		Alluvial/Gley	Forest	
Mean	**6.6**	**5.56**	**38**	**–0.4**				

Site	Temp	pH	EC	Alkalinity	Geology	Soil Type	Vegetation	Regime
HAF 11								
Min	0.0	4.42	41	–40.0	Frongoch	Complex	Mature	Perennial
Max	12.3	5.93	75	25.4	Mudstones	Peat/Podsol/	Coniferous	Small Stream
Range	12.3	1.51	34	65.4		Gley	Forest	
Mean	**6.2**	**4.96**	**59**	**–12.5**				
HAF 12								
Min	0.0	4.33	54	–53.2	Frongoch	Complex	Mature	Perennial
Max	14.0	5.75	81	26.1	Mudstones	Peat/Podsol/	Coniferous	Small Stream
Range	14.0	1.42	27	79.3		Gley	Forest	
Mean	**7.0**	**5.12**	**64**	**–7.9**				
HAF 13								
Min	0.2	3.58	36	–204.7	Gwestyn	Gley/Podsol	Mature	Ephemeral
Max	14.5	6.06	148	–48.5	Shales		Coniferous	Small Stream
Range	14.3	2.48	112	156.2			Forest	
Mean	**6.0**	**3.96**	**79**	**–129.2**				
HAF 14								
Min	0.1	4.12	25	–36.1	Gwestyn	Complex	Mature	Perennial
Max	13.4	6.89	89	44.7	Shales	Peat/Podsol/	Coniferous	Main River
Range	13.3	2.77	64	80.8		Alluvial/Gley	Forest	
Mean	**6.6**	**5.39**	**42**	**1.6**				
TAN 1								
Min	0.1	3.98	40	–89.7	Fan Shales	Complex	Felled &	Perennial
Max	15.1	5.79	66	15.3		Peat/Podsol	Replanted	Main River
Range	15.0	1.81	26	105.0			Coniferous	
Mean	**6.8**	**4.82**	**49**	**–21.6**			Forest	
TAN 2								
Min	1.3	4.25	36	–62.7	Fan Shales	Complex	Felled &	Perennial
Max	12.8	5.05	65	2.8		Peat/Podsol	Replanted	Small Stream
Range	11.5	0.80	29	65.5			Coniferous	
Mean	**6.8**	**4.67**	**47**	**–21.5**			Forest	
TAN 3								
Min	2.6	4.39	40	–41.4	Fan Shales	Complex	Felled &	Ephemeral
Max	11.3	4.76	59	–10.3		Peat/Podsol	Replanted	Small Stream
Range	8.7	0.37	19	31.0			Coniferous	
Mean	**6.6**	**4.64**	**49**	**–21.5**			Forest	
TAN 4								
Min	0.1	4.17	40	–62.5	Gwestyn	Complex	Mature	Perennial
Max	13.1	6.74	65	82.8	Shales	Peat/Podsol/	Coniferous	Main River
Range	13.0	2.57	25	145.3		Gley	Forest	
Mean	**6.4**	**5.36**	**51**	**2.2**				
TAN 5								
Min	0.1	4.14	46	–62.5	Gwestyn	Complex	Mature	Perennial
Max	18.0	6.68	68	90.2	Shales	Peat/Podsol	Coniferous	Main River
Range	17.9	2.54	22	152.6			Forest	
Mean	**6.9**	**5.35**	**54**	**2.8**				
TAN 6								
Min	0.1	3.76	44	–114.4	Gwestyn	Gley/Podsol	Felled	Ephemeral
Max	17.9	4.80	125	–29.2	Shales		Confierous	Small Stream
Range	17.8	1.04	81	85.2			Forest	
Mean	**6.9**	**4.10**	**73**	**–83.5**				

Site	Temp	pH	EC	Alkalinity	Geology	Soil Type	Vegetation	Regime
TAN 7								
Min	0.1	4.16	40	–77.2	Gwestyn	Complex	Felled	Perennial
Max	15.3	7.35	125	943.6	Shales	Peat/Podsol/	Coniferous	Main River
Range	15.2	3.19	85	1020.7		Alluvial	Forest	
Mean	**6.7**	**5.64**	**59**	**73.1**				
TAN 8								
Min	0.1	4.22	39	–49.9	Gwestyn	Complex	Felled	Perennial
Max	17.7	7.29	93	515.0	Shales	Peat/Podsol/	Coniferous	Main River
Range	17.6	3.07	54	564.9		Alluvial	Forest	
Mean	**7.1**	**6.13**	**61**	**119.6**				
HOR 1								
Min	0.2	4.32	29	–53.0	Fan Shales	Complex	Felled &	Perennial
Max	14.2	7.66	100	259.4		Peat/Podsol/	Replanted	Main River
Range	14.0	3.34	71	312.4		Gley	Coniferous	
Mean	6.8	5.97	44	20.5			Forest	
HOR 2								
Min	0.9	4.30	23	–31.6	Gwestyn	Peat/Podsol	Felled &	Perennial
Max	12.0	5.26	90	2.7	Shales		Replanted	Small Stream
Range	11.1	0.96	67	34.2			Coniferous	
Mean	**6.4**	**4.77**	**48**	**–13.9**			Forest	
HOR 3								
Min	0.1	4.30	24	–47.2	Gwestyn	Peat/Podsol/	Felled &	Perennial
Max	18.6	7.58	118	428.7	Shales	Alluvial	Replanted	Main River
Range	18.5	3.28	94	475.8			Coniferous	
Mean	**7.6**	**5.87**	**47**	**16.1**			Forest	
SEV 1								
Min	0.5	4.35	38	–36.1	Gwestyn	Complex	Mature	Perennial
Max	15.3	7.08	56	93.0	Shales	Alluvial/	Coniferous	Main River
Range	14.8	2.73	18	129.1		Peat	Forest	
Mean	**7.0**	**5.88**	**46**	**16.3**				
SEV 2								
Min	1.1	5.24	49	–14.5	Gwestyn	Podsol	Felled &	Perennial
Max	13.1	6.88	80	99.6	Shales		Replanted	Small Stream
Range	12.0	1.64	31	114.1			Coniferous	
Mean	**7.4**	**6.43**	**67**	**43.9**			Forest	
SEV 3								
Min	0.1	4.30	56	–65.1	Gwestyn	Podsol	Felled &	Perennial
Max	13.9	5.20	81	–5.8	Shales		Replanted	Small Stream
Range	13.8	0.90	25	59.3			Coniferous	
Mean	6.6	4.77	70	–22.3			Forest	
SEV 4								
Min	0.0	4.45	39	–42.1	Gwestyn	Complex	Mature	Perennial
Max	13.5	6.95	55	93.9	Shales	Alluvial/	Coniferous	Main River
Range	13.5	2.50	16	136.0		Peat/Podsol	Forest	
Mean	**6.2**	**5.80**	**45**	**14.4**				
SEV 5								
Min	0.0	4.52	38	–50.2	Frongoch	Complex	Mature	Perennial
Max	13.7	7.03	53	132.6	Mudstones	Alluvial/	Coniferous	Main River
Range	13.7	2.51	15	182.8		Peat/Podsol	Forest	
Mean	**6.1**	**5.90**	**45**	**23.2**				

Site	Temp	pH	EC	Alkalinity	Geology	Soil Type	Vegetation	Regime
SEV 6								
Min	0.0	4.53	36	–45.6	Frongoch	Complex	Mature	Perennial
Max	13.7	6.95	63	126.9	Mudstones	Alluvial/	Coniferous	Main River
Range	13.7	2.42	27	172.5		Peat/Podsol	Forest	
Mean	**6.0**	**5.89**	**46**	**20.1**				
SEV 7								
Min	0.7	5.12	43	–20.5	Frongoch	Podsol	Mature	Perennial
Max	13.6	6.87	99	97.6	Mudstones		Coniferous	Small Stream
Range	12.9	1.75	56	118.1			Forest	
Mean	**7.0**	**6.30**	**57**	**28.3**				
SEV 8								
Min	0.0	4.53	37	–40.0	Frongoch	Complex	Mature	Perennial
Max	14.0	7.04	55	130.4	Mudstones	Alluvial/	Coniferous	Main River
Range	14.0	2.51	18	170.4		Peat/Podsol	Forest	
Mean	**6.2**	**5.93**	**45**	**23.4**				

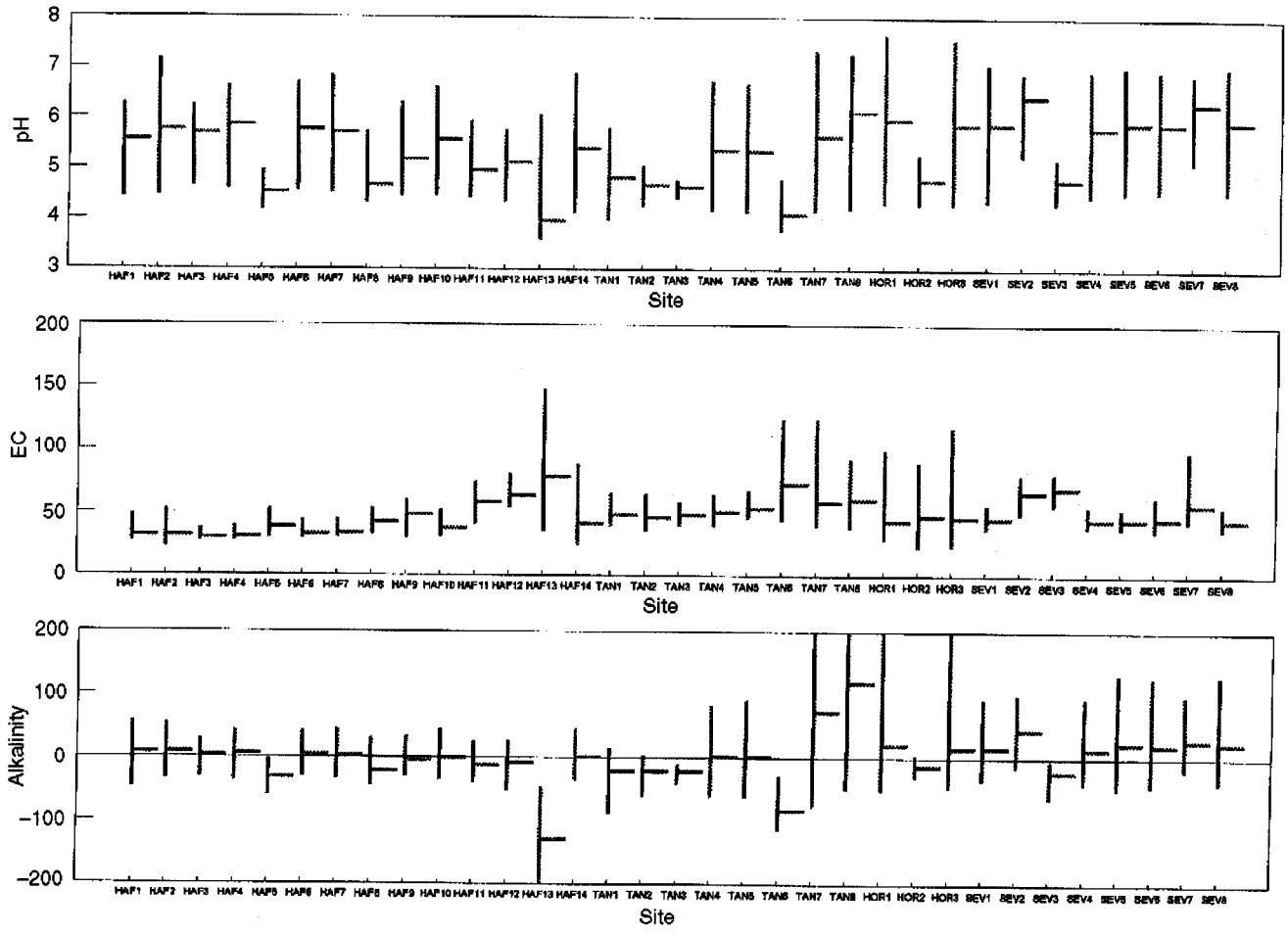

Fig. 13. *Box and Whisker plot of chemical variation in stream waters across the catchment.*
Figure description; Vertical lines on chart represent the range of values and the horizontal lines indicate the mean.

hydrological routing, residence times, reaction kinetics and volumetric processes, all operating at small scales.

The large variability observed has implications for the hydrochemical modelling of upland catchments. In the highly variable systems being studied here, the spatial and temporal scales at which the processes operate are so small that it is impractical to model in a deterministic way, due to the inherent complexity and the ease of over-parameterisation. Therefore, problems arise with catchments models due to over-simplification of the hydrological and hydrochemical processes operating (Christophersen, *et al.*, 1993; Neal, *et al.*, 1997a). The temporal variations in the Upper Severn catchment are relatively straightforward reflecting the flow conditions. However, the spatial variations require a more detailed understanding. Spatial variations in stream and ground water chemistry, linked to heterogeneous processes varying over small distances, are difficult to model without inordinately extensive field data. The difficulties of a model to represent stream and ground water chemistry at the intra-catchment level further suggests a need for the revaluation of catchment model structure (Neal, *et al.*, 1997d).

The nature of the variation in stream chemistry, as observed in the Upper Severn catchment, has ramifications for the use of critical load analysis in developing catchment management programmes. Problems associated with scale have been noted in the use of catchment characteristics to produce surface water acidification sensitivity maps (Hornung, *et al.*, 1995). Due to the inherent variability of within catchment chemistry, critical loads would need to be calculated on a sub-catchment basis to be a true representation of the catchment. The calculation of critical loads at these levels may not be practical. However, the use of simple determinations like alkalinity and pH may provide the basis of a suitable method.

Wider Comment

The results presented have demonstrated the value of simple water quality indicators (pH, alkalinity and conductivity) for examining soil-ground water relationships in upland catchments, the complexity of hydrological pathways and the way that water flowing along these pathways mixes. The results extend the hydrograph splitting technique of EMMA and the possibility of broadly using chemical finger printing in identifying areas of contrasting weathering. The results indicate clearly that the assumption of end member chemistries of fixed composition in space and time is not correct, furthermore, the river output signal does not contain enough information to represent the complexity of the inputs.

Clearly, the hydrochemical functioning of these upland

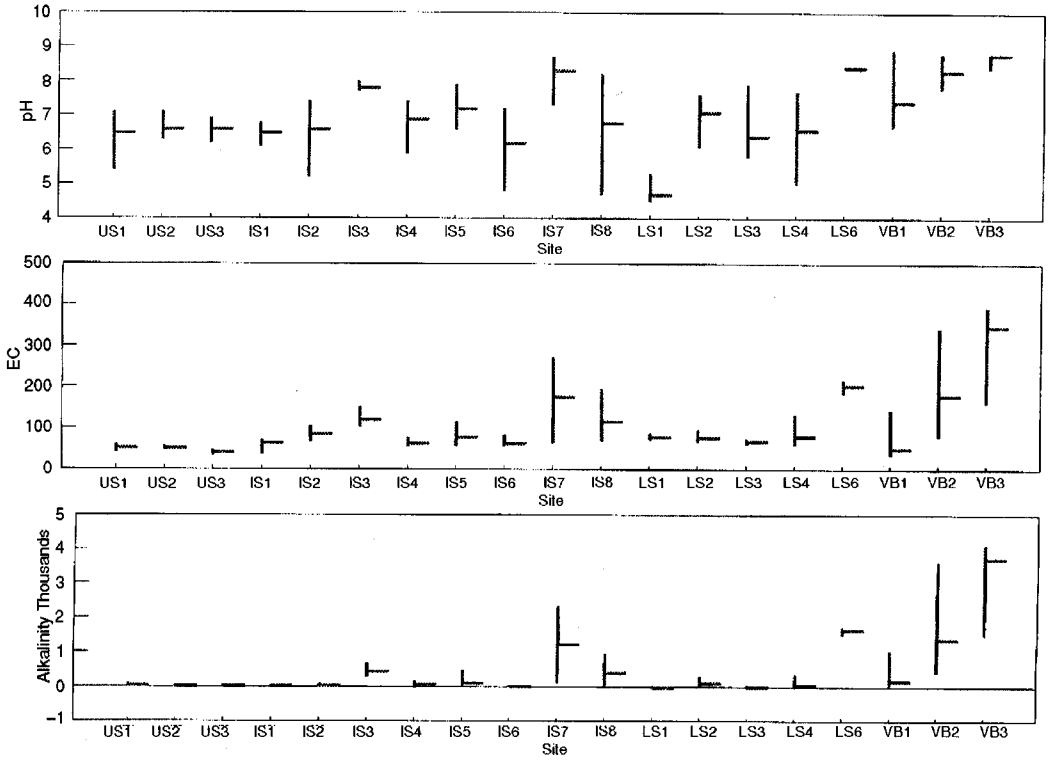

Fig. 14. *Box and Whisker plot of chemical variation in groundwaters across the catchment.*
Figure description; Vertical lines on chart represent the range of values and the horizontal lines indicate the mean values.

Table 3.

Site	Level (m)	Level (m) (AOD)	Temp	pH	EC	Alkalinity	pH (EDegassed)	pCO_2	HCO_3
US1									
Min	0.51	583.39	4.2	4.69	39	4.7	5.4	13	0
Max	2.90	585.78	11.9	5.83	60	103.1	7.1	159	71
Range	2.39	2.39	7.7	1.14	21	98.4	1.7	147	71
Mean	**1.00**	**585.29**	**7.3**	**4.91**	**52**	**45.0**	**6.5**	**82**	**23**
US2									
Min	8.66	568.77	6.2	5.08	47	1.4	6.3	4	4
Max	14.38	574.49	9.4	6.43	55	49.9	7.1	33	66
Range	5.72	5.72	3.2	1.35	8	48.5	0.8	29	61
Mean	**11.55**	**571.59**	**7.3**	**5.30**	**51**	**21.9**	**6.6**	**24**	**19**
US3									
Min	7.36	556.83	6.4	4.99	32	5.9	6.2	27	3
Max	13.75	563.22	8.7	5.41	46	48.3	6.9	65	43
Range	6.39	6.39	2.3	0.42	14	42.4	0.7	38	41
Mean	**10.34**	**560.25**	**7.4**	**5.13**	**40**	**25.7**	**6.6**	**40**	**20**
LS1									
Min	1.19	337.96	6.0	4.35	72	−36.5	4.5	1	0
Max	3.36	340.13	11.2	4.85	86	25.6	5.3	167	0
Range	2.17	2.17	5.2	0.50	14	62.2	0.7	165	0
Mean	**1.74**	**339.58**	**8.1**	**4.61**	**79**	**−12.0**	**4.7**	**23**	**0**
LS2									
Min	0.00	341.83	6.0	5.05	66	17.5	6.1	6	1
Max	1.97	343.80	11.0	6.45	95	292.2	7.6	143	258
Range	1.97	1.97	5.0	1.40	29	274.7	1.5	137	257
Mean	**0.62**	**343.18**	**8.3**	**5.89**	**77**	**114.4**	**7.1**	**22**	**100**
LS3									
Min	0.10	341.65	6.0	4.91	61	−12.7	5.8	14	0
Max	3.88	345.43	11.0	6.64	73	43.2	7.9	58	460
Range	3.78	3.78	5.0	1.73	12	55.9	2.1	44	460
Mean	**1.85**	**343.68**	**7.9**	**5.17**	**68**	**15.7**	**6.4**	**26**	**20**
LS4									
Min	1.80	344.41	6.0	4.75	60	−10.4	5.0	4	0
Max	6.07	348.68	9.9	6.25	132	340.9	7.7	107	335
Range	4.27	4.27	3.9	1.50	72	351.3	2.8	103	335
Mean	**4.91**	**345.58**	**8.0**	**5.28**	**80**	**50.9**	**6.6**	**32**	**46**
LS5									
Min	5.89	362.89	7.0	5.05	36	2.8	6.1	11	1
Max	9.74	366.74	8.5	5.62	70	41.4	6.8	41	36
Range	3.85	3.85	1.5	0.57	34	38.6	0.7	30	36
Mean	**8.38**	**364.25**	**7.8**	**5.37**	**64**	**20.4**	**6.5**	**18**	**15**
LS6									
Min	3.31	352.96	7.0	4.77	67	−3.4	5.2	16	0
Max	7.26	356.91	8.8	5.80	105	93.3	7.4	79	160
Range	3.95	3.95	1.8	1.03	38	96.7	2.2	63	160
Mean	**6.41**	**353.81**	**7.9**	**5.33**	**85**	**38.5**	**6.6**	**32**	**39**
VB1									
Min	1.10	348.20	6.1	4.54	35	24.2	6.7	27	28
Max	2.60	349.70	11.0	6.82	143	1030.0	8.9	2365	4947

Site	Level (m)	Level (m) (AOD)	Temp	pH	EC	Alkalinity	pH (EDegassed)	pCO_2	HCO_3
Range	1.50	1.50	4.9	2.28	108	1005.8	2.2	2337	4919
Mean	**1.95**	**348.84**	**8.3**	**5.64**	**50**	**169.2**	**7.4**	**106**	**522**
IS3									
Min	3.38	384.38	5.7	6.34	103	285.0	7.7	10	281
Max	5.83	386.83	10.4	6.78	150	678.8	8.0	29	668
Range	2.45	2.45	4.7	0.44	47	393.8	0.4	19	387
Mean	**4.32**	**385.88**	**8.0**	**6.61**	**120**	**445.4**	**7.8**	**18**	**438**
IS4									
Min	2.58	342.41	5.8	4.68	55	–15.5	5.9	14	0
Max	5.30	345.13	9.8	6.23	76	168.3	7.4	112	27
Range	2.72	2.72	4.0	1.55	21	183.8	1.6	99	27
Mean	**3.71**	**343.99**	**7.9**	**5.38**	**63**	**66.8**	**6.9**	**54**	**11**
IS5									
Min	1.91	346.96	6.0	5.02	56	21.4	6.6	17	20
Max	3.24	348.29	11.0	6.11	115	478.7	7.9	142	464
Range	1.33	1.33	5.0	1.09	59	457.4	1.3	125	445
Mean	**2.70**	**347.49**	**8.3**	**5.51**	**78**	**110.6**	**7.2**	**49**	**107**
IS7									
Min	0.76	355.70	6.5	5.36	64	120.9	7.3	62	114
Max	4.50	359.44	10.6	6.58	270	2319.8	8.7	157	3088
Range	3.74	3.74	4.1	1.22	206	2198.9	1.4	94	2975
Mean	**3.10**	**357.10**	**7.9**	**6.30**	**175**	**1223.8**	**8.3**	**92**	**1329**
IS6									
Min	1.02	356.38	5.9	4.57	56	–9.6	4.8	20	0
Max	4.90	360.26	11.1	5.27	82	45.9	7.2	103	83
Range	3.88	3.88	5.2	0.70	26	55.5	2.3	82	83
Mean	**2.82**	**358.46**	**8.1**	**4.84**	**63**	**18.6**	**6.2**	**66**	**11**
IS8									
Min	4.69	416.69	7.0	4.52	69	–19.8	4.7	8	0
Max	9.84	421.84	8.6	6.56	194	961.3	8.2	69	959
Range	5.15	5.15	1.6	2.04	125	981.1	3.5	61	959
Mean	**8.81**	**417.72**	**7.8**	**5.67**	**116**	**405.4**	**6.8**	**43**	**409**
LS6									
Min	1.25	338.30	6.5	6.94	184	1496.5	8.4	5	1483
Max	2.93	339.98	10.2	7.70	215	1699.2	8.4	31	1680
Range	1.68	1.68	3.7	0.76	31	202.7	0.1	26	197
Mean	**2.44**	**338.79**	**8.2**	**7.35**	**202**	**1652.1**	**8.4**	**12**	**1635**
VB2									
Min	0.88	348.59	5.3	6.72	80	415.1	7.8	1	414
Max	2.40	350.11	12.4	8.36	342	3600.5	8.8	66	3530
Range	1.52	1.52	7.1	1.64	262	3185.4	0.9	66	3116
Mean	**1.89**	**349.10**	**8.4**	**7.25**	**178**	**1383.0**	**8.3**	**16**	**1367**
VB3									
Min	0.00	353.04	5.0	6.69	161	1505.9	8.4	4	1491
Max	0.77	353.81	15.5	7.80	393	4099.8	8.8	129	4041
Range	0.77	0.77	10.5	1.11	232	2593.9	0.4	126	2549
Mean	**0.07**	**353.74**	**8.5**	**6.98**	**347**	**3717.4**	**8.8**	**64**	**3690**

catchments is more complex than current environmental models suggest. While this should concern environmental managers and modellers alike, the variability observed may point the way for practical methods of alleviating the problems associated with acid deposition and landuse change (See Neal, *et al.*, 1997d).

This paper extends the optimistic theme for improving water quality by groundwater manipulation and modifying water flow pathways in the soil by physical methods as presented earlier in this issue (Neal, *et al.*, 1997d) and previous publications (Neal, *et al.*, 1997 b,c). However, given the heterogeneous nature of upland catchments, such techniques must be based on field measurements rather than using the over-simplistic and inappropriate modelling methods that are currently used.

References

Billet, M.F., Lowe, J.A.H., Black, K.E. & Cresser, M.S. 1996. The influence of parent material on small-scale spatial changes in streamwater chemistry in Scottish upland catchments. *J. Hydrol.*, **187**, 311–331.

Blöschl, G. and Sivapalan, M. 1995. Scale issues in hydrological modelling: A review. *Hydrol. Processes*, **9**, 251–290.

Breward, N. 1990. *Geochemical cycling processes involving major and trace elements at Plynlimon, Mid-Wales.* PhD Thesis. Dept. of Earth Sciences, University of Leeds, Leeds, UK. 565 pp.

Christophersen, N., Neal, C. and Hooper, R.P. 1990. Modelling streamwater chemistry as a mixture of soil water endmembers—a step towards second generation acidification models. *J. Hydrol.*, **116**, 307–321.

Christophersen, N., Neal, C. and Hooper, R.P. 1993. Modelling the hydrochemistry of catchments: a challenge for the scientific method. *J. Hydrol.*, **152**, 1–12.

Cosby, B.J., Hornberger, G.M. and Galloway, J.N. 1985. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Wat. Resour. Res.*, **21**, 51–63.

Davies, T.D., Tranter, M., Wigington, P.J. & Eshleman, K.N. 1992. Acidic episodes in surface waters in Europe. *J. Hydrol.*, **132**, 25–69.

Harriman, R., Likens, G.E., Hultberg, H. and Neal, C. 1994. Influence of management practices in catchments on freshwater acidification: Afforestation in the United Kingdom and North America, *In:* Steinberg C.E. and Wright, R.F., eds. *Acidification of Freshwater Ecosystems: Implications for the Future.* Wiley, Chichester, UK. pp. 83–101.

Hornung, M., Bull, K.R., Cresser., Ullyett, J., Hall, J.R., Langan, S., Loveland, P.J. & Wilson, M.J. 1995. The sensitivity of surface waters of Great Britain to acidification predicted from catchment characteristics. *Environ. Poll.*, **87**, 207–214.

Kirby, C., Newson, M.D. and Gilman, K., eds. 1991. Plynlimon Research: The first two decades. *Institute of Hydrology.* Report No.109.

Neal, C. 1988a. Bicarbonate estimation from alkalinity determinations for neutral to acidic low alkalinity natural waters: theoretical considerations. *Hydrol. Sci. Bull.*, **33**, 619–624.

Neal, C. 1988b. Determination of dissolved CO_2 in upland streamwater. *J. Hydrol.*, **99**, 127–142.

Neal, C., Robson, A. and Smith, C.J. 1990a. Acid neutralization capacity variations for the Hafren forest stream, Mid-Wales: inferences for the hydrological processes. *J. Hydrol.*, **121**, 85–101.

Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M. 1990b. Hydrochemical variations in Hafren forest stream waters, Mid-Wales. *J. Hydrol.*, **116**, 185–200.

Neal, C., Smith, C.J. and Hill, S. 1992a. Forestry impact on upland water quality. *Institute of Hydrology.* Report No.119.

Neal, C., Fisher, R., Smith, C.J., Hill, S., Conway, T., Ryland, G.P. and Jeffrey, H. 1992b. The effects of tree harvesting on stream-water quality at an acidic and acid-sensitive spruce forested area. *J. Hydrol.*, **135**, 305–319.

Neal, C., Robson, A.J. and Christophersen, N. 1997a. Towards coupling hydrological, soil and weathering processes within a modelling perspective. *In:* Saether, O.M. & Caritat, P. eds. *Geochemical Processes, weathering and groundwater recharge in catchments.* A.A. Balkema, Rotterdam. 395pp.

Neal, C., Hill, T., Alexander, S., Reynolds, B., Hill, S., Dixon, A.J., Harrow, M., Neal, M. & Smith, C.J. 1997b. Stream water quality in acid sensitive UK upland areas; an example of potential water quality remediation based on groundwater manipulation. *Hydrol. Earth System Sci.*, 1, 185–196.

Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow, M., Neal, M., Wilkinson, J. & Reynolds, B.1997c. The occurrence of groundwater in the Lower Palaeozoic rocks of upland Central Wales. *Hydrol. Earth System Sci.*, 1, 3–18.

Neal, C., Hill, T., Hill., S. and Reynolds, B. 1997d. Acid neutralisation capacity measurements in surface and ground waters in the Upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways. *Hydrol. Earth System Sci.*, 1, 687–696.

Pitcairn, C.E.R (ed). 1994. Critical Loads of acidity in the United Kingdom, *C.L.A.G. Summary Report.* Institute of Terrestrial Ecology, pp.61.

Robson, A.J., Neal, C., Hill, S. and Smith, C.J. 1992. Short-term variations in rain and stream water conductivity at a forested site in Mid-Wales—implications for water movement. *Sci. Total Environ.*, **119**, 1–18.

Robson, A.J. 1993. *The use of continuous measurement in understanding and modelling the hydrochemistry of the uplands.* PhD Thesis. University of Lancaster, Lancaster, UK. 278 pp.

Robson, A.J., Neal, C., Hill, S. and Smith, C.J. 1993. Linking variations in short- and medium-term chemistry to rainfall inputs—some observations at Plynlimon, Mid-Wales. *J. Hydrol.*, **144**, 291–310.

Robson, A.J. and Neal, C. 1996. Water quality trends at an upland site in Wales, UK, 1983–1993. *Hydrol. Processes*, **10**, 183–203.

Appendix 1

This Paper	(Neal, *et al.*, 1992a; Neal, *et al.*, 1997b)
Stream Sites	**Alternative Names**
HAF1	
HAF2	Upper Hafren
HAF3	Arwystli
HAF4	
HAF5	
HAF6	
HAF7	
HAF8	
HAF9	
HAF10	
HAF11	
HAF12	
HAF13	E4, Tan North
HAF14	Afon Hafren Flume
TAN1	
TAN2	
TAN3	
TAN4	
TAN5	
TAN6	E5, Tan South
TAN7	Tanllwyth Flume
TAN8	
HOR1	Upper Hore Flume
HOR2	South 2 Hore
HOR3	Lower Hore Flume
SEV1	
SEV2	E1
SEV3	
SEV4	
SEV5	
SEV6	
SEV7	E3
SEV8	Severn Trapezoidal Flume